

Bonding of H in O vacancies of ZnO

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We investigate the bonding of H in O vacancies in ZnO using density functional calculations. We find that H is anionic and does not form multicenter bonds with Zn in this compound.

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ZnO is of importance as an extremely fast inorganic scintillator material when doped with Ga or In. It is useful in alpha particle detection, e.g. for devices such as deuterium-tritium neutron generators used in radiography.^{1,2,3,4,5,6} In this application, H treatment has been shown to improve properties. ZnO has also attracted much recent attention motivated by potential applications as an oxide electronic material,^{7,8,9,10} and in optoelectronic and lighting applications.^{11,12,13,14,15} H has been implicated as playing an important role in the electronic properties for ZnO for those applications as well.^{16,17,18} From a fundamental point of view, the behavior, and especially bonding of H, is of great interest; H plays an exceptionally important role in chemistry, and shows unique bonding characteristics. For example, it readily forms compounds where it behaves as a halogen ion and forms structures similar to fluorides, such as rutile, perovskite, rocksalt, etc.,^{19,20,21} and at the same time readily occurs a cation in other chemical environments. Polar covalent bonds involving H and hydrogen bonds are central to much of organic chemistry as well the properties of important substances such as water.²² Thus the recent report by Janotti and Van de Walle (JV) that H forms a new type of strong multicenter bond in O vacancies in ZnO is of wide ranging interest.²³

In this paper, we present standard local density approximation (LDA) calculations of the electronic properties and structure of H containing O vacancies in ZnO. We do not find the multicenter covalent bonds claimed by JV, and instead characterize the behavior of H as quite conventional in that it occurs as an anion on the anion site in a polar crystalline environment.

Our calculations were done within the standard local density approximation using the general potential linearized augmented plane wave (LAPW) method, including local orbitals.^{24,25} Specifically, we constructed a 72 atom 3x3x2 wurtzite supercells of ZnO, with one O atom removed and replaced by H. The calculations were done using the bulk lattice parameters of ZnO, but the internal coordinates of all atoms in the supercell were fully relaxed. No symmetry was assumed in the relaxations. The LAPW method is an all electron method that makes no shape approximations to either the potential or charge density. It divides space into non-overlapping atom centered spheres and an interstitial region. The method then employs accurate basis sets appropriate for each region.²⁴ In the present calculations, LAPW sphere radii of $2.0 a_0$,

$1.6 a_0$ and $1.2 a_0$ were used for Zn, O, and H respectively, along with a basis set consisting of more than 8500 LAPW functions and local orbitals. Convergence tests were done with a larger basis set of approximately 12000 functions, but no significant changes were found. The relaxations were done without any imposed symmetry, with a 2x2x2 special \mathbf{k} -point zone sampling. A sampling using only the Γ point was found to yield slightly different quantitative results, due to the limited size of our supercell, but would lead to the same conclusions. The calculated value of the internal parameter is $u=0.119$, which agrees almost exactly with the experimental value. The densities of states used to analyze the electronic properties were obtained using the linear tetrahedron method based on eigenvalues and wavefunctions at 36 \mathbf{k} -points in the half zone (\mathbf{k} and $-\mathbf{k}$ are connected by time reversal).

In our relaxed structure for a neutral cell, we find that H occurs in a slightly asymmetric position, with three Zn neighbors at 2.03 \AA , and one Zn neighbor (the one along the c -axis direction) at 2.17 \AA . For the singly charged cell, we obtain a very similar result, specifically three Zn neighbors at 2.02 \AA , and the apical Zn at 2.21 \AA . In the following, we focus on the neutral cell except as noted.

Fig. 1 shows the projection of the electronic density of states onto the H LAPW sphere, of radius $1.2 a_0$. The Fermi energy for our neutral cell lies at a position one electron per cell into the conduction bands, corresponding to the valence difference of one between O and H. As may be seen, there are two prominent peaks in the H component of the density of states, one, denoted "B", at $\sim -8 \text{ eV}$ with respect to the Fermi level (-6 eV with respect to the valence band maximum), and the other, denoted "A", high in the conduction bands at $\sim 6 \text{ eV}$. JV identified these peaks, "B" and "A", respectively, as the bonding and antibonding combinations of metal and H orbitals giving rise to the multicenter bond. In addition, there is significant H s character distributed over the valence bands, especially near the valence band maximum. We note that the very large bonding-antibonding splitting of 14 eV implied by the assignment of JV indicates extremely strong covalent bonds, which is somewhat surprising considering the Zn-H distances. In any case, such a large covalent gap would imply that the bonding and antibonding states should have mixed character. In other words, the bonding state should be of roughly half H s character, while the remaining H $1s$ character should occur in the unoccupied antibonding level, so that the oc-

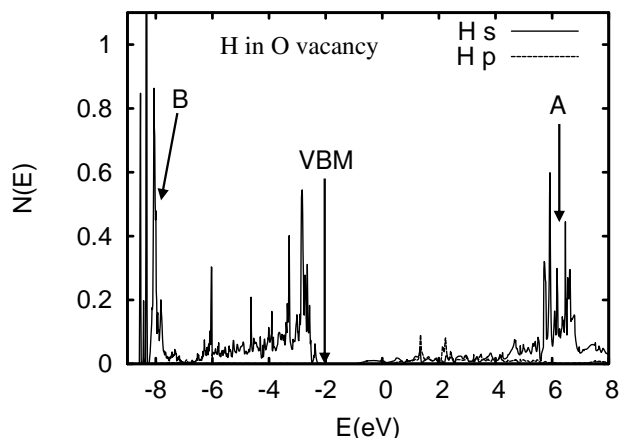


FIG. 1: Projection of the electronic density of states onto the s and p components inside the H LAPW sphere, radius $1.2 a_0$, for the 72 atom neutral cell. The two peaks identified by JV as bonding and antibonding combinations are indicated by “B” and “A”, respectively. The Fermi level lies in the conduction bands. The position of the valence band maximum is denoted by “VBM” (note that the LDA strongly underestimates the 3.3 eV band gap of ZnO).

cupancy of the H $1s$ orbital should be roughly 1 e, and certainly significantly less than 2 e.

To analyze the bonding further it is convenient to compare the charge density with an ionic model, as was done for some alanates.^{30,31} As mentioned, H is known to enter some solids as an anion, including tetragonal MgH_2 .²⁶ ZnH_2 also exists though it is not as well characterized.³² Furthermore, the simplest hydride, LiH, is of this ionically bonded type and includes H^- anions coordinated by six metal atoms.^{33,34} In these hydrogen anion based materials, the negative H ion is stabilized by the Ewald field. In fact, the importance of the Ewald field is one of the essential differences between chemistry in solid state and the chemistry of molecules. The long range Coulomb interaction stabilizes ionic bonding for species that would generally be largely covalent in small molecules, and in particular stabilizes anions such as O^{2-} and H^- , which are common in solid state chemistry but much less so in gas phase molecules. This stabilization by the Ewald field is reflected in the variability of the effective size of H in crystal structure data for anionic hydrides.^{27,28,29} In view of the common occurrence of H as an anion in many metal hydrides, it would not be surprising if H^- were stabilized by the Ewald field of an anion vacancy in a polar crystal such as ZnO. Thus we consider an ionic model, based on the charge density of a H^- ion stabilized by the Ewald field, as simulated by a Watson sphere,³⁵ as in Ref. 31. For such a H^- ion, 0.525 e out of 2.0 e, i.e. $\sim 26\%$ of the charge, is inside a radius of $1.2 a_0$, so the majority of the charge is outside. Because of the small sphere radius used for H in our calculations the amount of charge in-

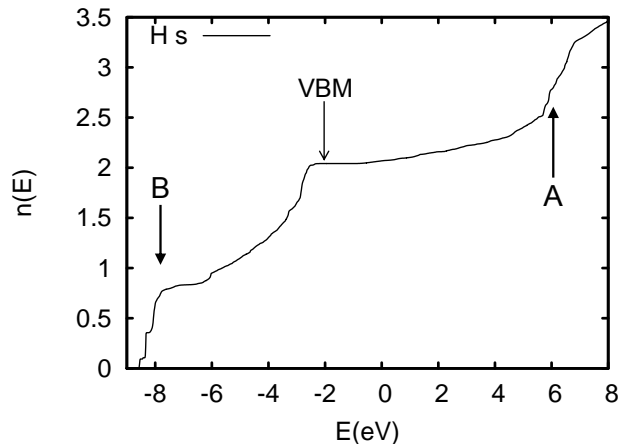


FIG. 2: Integration of the projection of the H s projected density of states as in Fig. 1 normalized according to the fraction of charge inside a $1.2 a_0$ sphere for a Watson sphere stabilized H^- anion (see text).

side the sphere is only weakly dependent on the Watson sphere radius, which reflects the environment. For a non-spin polarized neutral H in free space as described in the LDA, 0.378 e (38%) would be inside a radius of $1.2 a_0$, showing that there is a strong dependence on the charge state, though not precise proportionality. Fig. 2 shows the integral of the H s character as a function of energy normalized by the fraction of the H^- charge inside a $1.2 a_0$ sphere (0.525/2). Over the valence band region the p contribution is less than 2%, and the d contribution is less than 0.2%. The conduction bands, which are more Zn sp derived, show a larger proportion of H p character, as may be seen in Fig. 1. Thus the charge inside the sphere, which comes from the occupied valence bands, is mainly due to H s states, and not from orbitals on neighboring atoms.

Using the ionic model for H^- , i.e. incorporating the factor of 0.525/2 as the fraction of charge inside the H LAPW sphere, and integrating, one finds that the peak “B” contains ~ 0.8 H s electrons. Integrating over the remaining valence bands brings the H s count to 2.0 electrons, i.e. what is expected for H^- . This leads to an interpretation of the electronic structure, where the peak “B” comes from the H $1s$ state. This hybridizes with valence band states, which have mixed Zn d and O p character. The second peak “A”, 14 eV higher, is then the H s resonance. This is a very reasonable position for the resonance of H^- . In particular, the H^- resonance of atomic H^- is at ~ 14.5 eV.^{36,37,38} JV emphasized the shape of the charge density associated with the states in the peak “B” and argued for bonding based partly on real space images of this charge. As mentioned, in our projected density of states we find that this peak contains 0.8 s electrons (i.e. 40% H s character), which would

be consistent with a bonding orbital. However, the hybridization is with other occupied states, and when the integration is done over all the valence bands, we find 2 s electrons, consistent with H^- . We emphasize that mixing of occupied states does not contribute to the energy, and that such hybridizations do not constitute bonds. Our calculated binding energy relative H_2 and a relaxed neutral supercell with an O vacancy is 87 kJ/mol H.³⁹ This may be an overestimate due to LDA errors,⁴⁰ but in any case is much smaller than the binding that would be suggested by a 14 eV bonding-antibonding splitting.

We also calculated the positron wavefunction and lifetimes for ZnO with an O vacancy and with the H containing O vacancy. This was done using the LAPW method in the full inverted self-consistent Coulomb potential plus the correlation and enhancement factors of Boronski and Nieminen⁴¹ as calculated from the full charge density. We obtain a bulk positron lifetime for ZnO of 144 ps, which is at the lower end of the experimental range. Reported experimental values are 151 ps (Ref. 42), 170 ps (Ref. 43), 141 ps - 155 ps (Ref. 44), and 182 ps (Ref. 45). Significantly, positrons, which are positively charged, tend to localize in voids and in sites that are favorable for cations, and localize weakly if at all in anion sites, due

to the unfavorable Coulomb potential. We do not find positron localization at the O vacancy in our ZnO supercell, indicating that the O is indeed an anion as expected, nor do we find positron localization or a significant lifetime increase in the cell with a H containing O vacancy. We also find no significant change in lifetime for H in an O vacancy within a charged supercell with one electron removed. In contrast, we obtain a bound positron state for Zn vacancies, both with and without H, reflecting the fact that Zn is on a cation site. The calculated lifetime in a supercell with a Zn vacancy is 212 ps, while with a H filled Zn vacancy we obtain 175 ps (in this case H bonds to a single adjacent O to form a hydroxyl like unit with H-O bond length of 1.01 Å).⁴⁶

To summarize, we have performed density functional calculations for ZnO supercells with both empty and H filled O vacancies. Based on an analysis of the electronic structure we do not find any evidence for hydrogen multicenter bonds, but rather find that H occurs as H^- .

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